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LAWS OF CATIONIC POLYMERIZATION OF 9-VINILCARBAZOLE UNDER THE INFLUENCE OF TRITILLIUM SALTS

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Kinetic laws of cationic polymerization of 9-vinylcarbazole under the influence of $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ in a solution $CHCl_3$ at 20 °C have been studied. Kinetic of the process was studied by setting the stopped flow method with recording in IR region. The behavior of the studied system corresponds to the model of «quasi-alive» polymerization. It is supposed that the most probable type of active particles is solvate separated ion pairs. The efficient value of circuit growth constant is calculated.

9-Vinylcarbazole (VC) possesses very high reactivity in cationic polymerization under the influence of different initiators. In papers [1, 2] it is shown that carbenium ion stable salts, among them hexachlorineantimonates $SbCl_6^-$ and hexafluorarsenates AsF_6^- tropylium $C_7H_7^+$ and tritilium Ph_3C^+ are efficient initiators of olefin series polymerization. Owing to high stability of such salts initiation of the most active monomer polymerization is only possible that was confirmed at studying polymerization of 9-vinylcarbazole (VC) and other monomers [3–9]. Under the influence of stable organic cations initiating systems acting quantitatively and allowing estimating absolute velocities of VC cationic polymerization could be developed.

It is reputed [10] that at VC polymerization with $C_7H_7^+SbCl_6^-$ or $Ph_3C^+AsF_6^-$ initiating occurs almost instantly by direct joining carbocation to monomer therefore, studying such polymerization only chain growth process could be traced. However, even chain growth in this case occurs very rapidly that requires applying special analyses.

It is known that medium influence is one of determining factors on which rate constant of single stages of ionic polymerization depend [11–13]. Stabilization of formed ionized particles and change of active centre reactivity influence most significantly. Large dipole moment of ion pairs result in their strong interaction with polar molecules including molecules of polar solvents. Solvate separated ion pairs exist only in the media where at least one free ion is coordinated with solvent molecules. In the case of weakly solvating solvents their function may be fulfilled to some degree by monomers changing dielectric constant of the medium or by other components taking part directly in polymerization that appears in changing reaction kinetic order by these substances.

It is obvious that ion pairs and free ions may be of different activity. Usually ion pairs are inferior significantly to free ions in activity. So, for example, for polymerization of 9-vinylcarbazole in solution CH_2Cl_2 under the influence of $Ph_3C^+SbCl_6^-$ at 20 °C velocity constants of growth of free ion and ion pair respectively equal to $6\cdot10^5$ and $5\cdot10^4$ $l\cdot mole^{-1}\cdot s^{-1}$ [6]. According to the data [5] the corresponding values may differ by several orders. It is stipulated by higher efficient density of a free cation charge in comparison with the respective ion pairs [14, 15].

Polymerization with ion pairs is several times slower and it is more convenient for studying in this regard owing to a large number of available analyses. VC polymerization with $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ in solution $CHCl_3$ at 20 °C was studied. Process kinetic was studied with the help of the device of stopped flow method (SFM) with registration in IR region [16–19].

9-Vinylcarbazole obtained by the method [20] was crystallized twice from ethanol without acid admixtures, dried in vacuum drying chamber and stored in darkness. T_{MLT}=63,5...64,0 °C. Content of the main substance by the method of hydrolytic oximation [21] is not less than 99,8 %.

Chloroform was clarified by shaking with concentrated acetic acid, washed with weak alkali solution then with water and dried over CaH_2. After distillation solvent with T_{BOIL}=61,0...61,2 °C was stored over raw CaH_2.

Tritylchloride of «AP» type was applied without additional purification; solutions of the required concentration were prepared in dry solvent and stored in a box with inert atmosphere.

Diethylaluminumchloride (DEAC) was solved in a dry solvent and concentration of the obtained solution was determined by chelatometric titration with dithizone [22]. Process solutions were prepared by diluting the main solution with dry solvent to the required concentration. All works with DEAC were carried out in the box with inert atmosphere.

Thermogravimetric and differential-thermal analyses of the obtained polymers were carried out at the device SDT Q600. Diffractograms were recorded at the device DRON-2.0 ($Cu K_\alpha$ is the radiation filtered with nickel). Polymer samples in the form of thin films or powder floated into a cavity of atmospheric material were used. Curves of turbidimetric titration were taken at the device UNICO 1201 with the help of titration adapter TI. Standard cavities with thickness of 1,5 cm and volume of 30 ml were used.

To study VC polymerization process under the influence of DEAC the device of stopped flow method (SFM) with registration in spectrum IR-region was used (Fig. 1). The device represents an adapter to IR-spectrophotometer Specord 71 IR and installed in spectrophotometer cavity chamber at the place of standard removable cavity holder. In this connection the

adapter outer dimensions were chosen on the basis of sizes of spectrophotometer cavity chamber, simplicity of the device assembling and servicing. All parts contacting process solutions are made of teflon, titanium or glass.

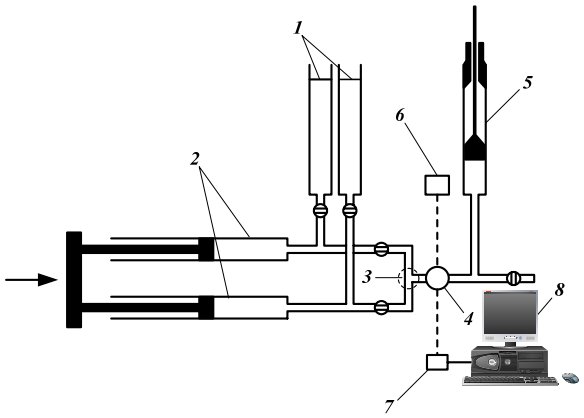

Fig. 1. *Diagram of the device for studying VC polymerization kinetics by the stopped flow method*

Structurally the device consists of measuring cell – 4 with volume 1 ml with glasses of CaF_2, mixing unit – 3, batching – 2 and shut-off – 5 piston mechanisms.

Solutions of monomer and initiator were prepared in inert atmosphere (dry clarified argon) and after thermostating were placed into reservoirs – 1 from which they entered batching piston mechanisms – 2. Measuring cell – 4 was preliminary filled up with dry solvent. Recording system was switched on and through the mixing unit – 3 solutions were injected into measuring cell accompanying by abrupt flow stop in shut-off piston mechanism – 5. Observation cell was lighted through the monochromator of spectrophotometer – 6. After signal transformation with ADC – 7 and its transfer into computer – 8 the kinetic curve may be recorded in wide time interval. Recording system start was synchronized at agent supply into observation chamber.

When recording unit showed that the reaction was fully completed the measuring cell was washed with dry solvent to achieving initial value of optical density.

Recording procedure was repeated several times for one and the same set of monomer and initiator concentrations. Chloroform was chosen as a solvent for carrying out kinetic measurements at SFM device as it does not have its own absorption bands in the researched spectral region (1700...1600 cm^{-1}).

To calculate reaction velocity constants on the basis of the results obtained at SFM device the observation cavity was calibrated and extinction coefficient of absorption band of VC vinyl bond valence vibration at ν=1656 cm^{-1} used for quantitative analysis was determined. It was shown that in monomer concentration region from $2{,}6\cdot10^{-3}$ to $2{,}6\cdot10^{-2}$ mole/l for absorption band at ν=1656 cm^{-1} the Lambert-Beer law is fulfilled:

$$D_{1656} = \varepsilon_{1656} lc,$$

where ε_{1656} is the coefficient of molar extinction, l/(mole·cm); l is the thickness of the cavity, cm; c is 9-vinylcarbazole concentration, mole/l.

The determined value of molar termination coefficient of valence vibration band of VC vinyl bond turned out to be equal to 195±2 l/(mole·cm). Thus, the bond between absorption band optical density at ν=1656 cm^{-1} and monomer concentration in chloroform solution may be expressed in the following way:

$$c = \frac{D_{1656}}{\varepsilon_{1656} l}.$$

Polymerization was carried out at initial concentrations of initiator and monomer $1{,}5\cdot10^{-5}$...$6{,}1\cdot10^{-5}$ and $1{,}6\cdot10^{-2}$...$2{,}6\cdot10^{-2}$ mole/l respectively. Kinetic curves were obtained by recalculation of optical density dependences on time τ, recorded at the SFM device by the formula

$$c = \frac{D_{1656}}{39{,}0 \pm 0{,}4}.$$

The reaction lasted ≈30 s. Dependence $\ln\frac{c_0}{c}$ on time (typical curves are presented in Fig. 2) is linear after a short induction period. The reaction has the first order by monomer and induction period indicates the fact that «slow» initiation is realized in the system [23–25].

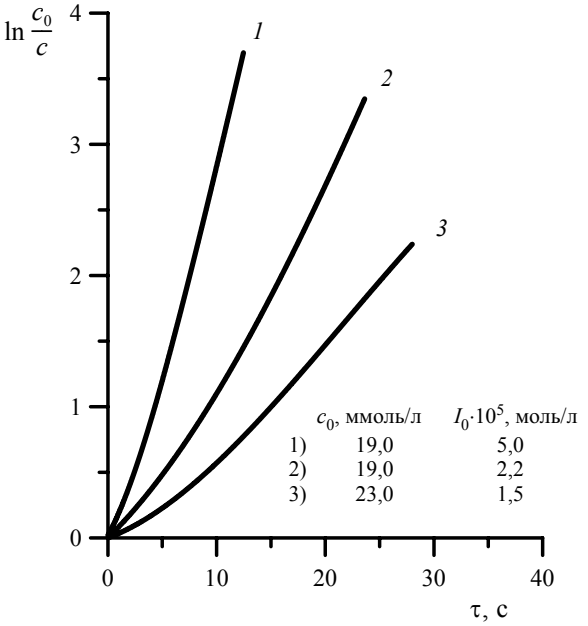

Fig. 2. *Dependence of the first order for VC polymerization (initial concentration c_0) under the influence of $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ (initial concentration I_0)*

The first order of the reaction relative to monomer is observed up to complete spent of the latter that indicates practically full absence of chain termination reaction. Moreover, adding new portion of monomer the reaction went on practically at the same rate that indicates presence of «live chains» in the given system [26–29]. In this regard the behavior of the given system coincides with the system VC-DEAC-chloroform studied before [17, 19]. However, kinetic laws have certain differences that implies slightly different mechanism of active centre formation.

In the given case stable organic cation Ph_3C^+ which is formed after reaction of equivalent quantities of Ph_3CCl and DEAC is polymerization active centre. However, presence of counterion $Al(C_2H_5)_2Cl_2^-$ which in comparison with hexafluorarsenates, hexaluorantimonates and suchlike inorganic counterions with low nucleophility [3–9] binds fully organic cation results in the fact that the most probable type of active centre type are solvate segregated ion pairs or even complex between VC and contact ion pair.

Chain growth in this case may be presented as competition of monomer, solvent and counterion around electrophylic centre [30–32]. Exchange interaction of ion pair segregated by solvent and monomer result in resolvation of ion pair and its expansion in the direction of counterion (Fig. 3).

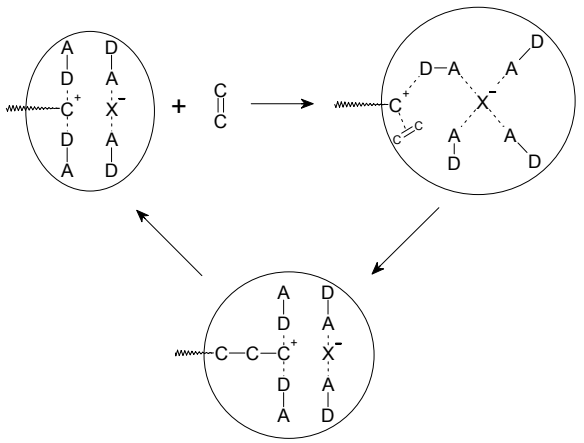

Fig. 3. *Exchange interaction of ion pair with monomer*

Exchange interaction between counterion and growing carbenium ion may be controlled by a charge and should depend on efficient electrophility of the latter.

At high cation electrophility (aliphatic vinyl monomers) and high counterion nucleophility ($CF_6^- \gg Cl^- \gg Br^- > I^-$) polymerization does not occur. Monomers forming resonant-stabilized cations with low electrophility (for example, vinyl ethers, 9-vinylcarbazole, dienes, p-methoxysterol) may be polymerized with counterions with low nucleophility (for example, SbF_6^-, AsF_6^-) at least at low temperatures with relatively small chain transfer. It is considered that in this case chain grows considerably through free solvated ions. At presence of counterions with relatively high nucleophility (for example, Br^-, I_{n+1}^-, $F_3CCO_2^-$, and other) these monomers are also capable to polymerization and probably general structure of active formation solution decreases potential energy so far as [33] in comparison with chain transfer to monomer its wedging into ion pair gets an advantage (Fig. 3).

Accepting the fact that practically the whole initiator turns into active centers and that relatively small amount of them die at polymerization an active center concentration may be considered to conform to initiator initial concentration:

$$P^* \simeq I_0.$$

Then velocity constant of polymer chain growth may be calculated from the ratio:

$$k_P = \frac{k_{НАБ}}{I_0},$$

where $k_{НАБ}$ is the observed velocity constant of pseudo-first order, s^{-1}; I_0 is the original concentration of initiator, mole/l. The obtained experimental results of studying VC polymerization under the influence of $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ in solution of $CHCl_3$ at 20 °C are given in the Table.

Table. *VC polymerization under the influence of $Ph_3C^+Al(C_2H_5)_2Cl_2^-$*

C_0, milimole/l	$I_0 \cdot 10^5$, mole/l	$k_{НАБ}$, s^{-1}	$k_P \cdot 10^{-3}$, $l \cdot mole^{-1} \cdot s^{-11}$
26,0	1,50	0,0985	6,57
26,0	2,00	0,1365	6,83
26,0	3,80	0,2754	7,25
26,0	4,20	0,2756	6,56
26,0	5,60	0,442	7,89
23,0	1,50	0,0949	6,33
23,0	2,50	0,1869	7,48
23,0	4,20	0,2992	7,12
21,0	1,50	0,0929	6,19
21,0	1,80	0,1291	7,17
21,0	2,50	0,1881	7,52
21,0	4,20	0,2802	6,67
21,0	4,60	0,3347	7,28
21,0	5,20	0,3808	7,32
19,0	2,20	0,1768	8,03
19,0	3,20	0,2416	7,55
19,0	5,00	0,3505	7,01
19,0	6,10	0,4858	7,96
16,0	1,80	0,1306	7,26
16,0	2,20	0,1460	6,64
16,0	3,80	0,2703	7,11
16,0	5,20	0,3430	6,60

It is considered that equilibrium between free ions and ion pairs in solution results in changing values k_P depending on monomer initial concentration [7]. However, it is seen from the obtained data that only one of two types of active particles mainly contributes to values k_P as values k_P do not practically change in the Table. We consider that ion pair should be such active particle as in our case stable organic cation contains much more nucleophilic counterion in comparison with AsF_6^-or $SbCl_6^-$. Temperature influences greatly the values of dissociation constant magnitude of tritylium salts [9, 34, 35]. When temperature increases the efficient value of dissociation constant decreases that in our case results in the fact that the main type of active particles in the given system are contact and solvate separated ion pairs, taking into account presence of more nucleophilic counterion.

The dependence of the observed constant of pseudo-first order of VC polymerization on original concentration of initiator is given in Fig. 4. The value of chain growth constant at ion pairs $k_P^{\mp}$ equal to $(7,2 \pm 0,2) \cdot 10^3$ $l \cdot mole^{-1} \cdot s^{-1}$ was found from the latter; the correlation coefficient for this dependence equal to 0,987.

According to the data of turbidimetric titration the unimodal molecular-mass distribution is typical for the obtained polymer samples and the tendency to narrowing molecular-mass distribution depending on process duration is observed; it may indicate indirectly the absence of chain temptation reaction.

It follows from the data of X-ray structure analysis that temperature influences mainly the crystallinity of the obtained polyvinylcarbazole samples. Wide amorphous halo with maximum at 2θ=20...21° and weak reflection peak at 2θ=8,1°, referred to inerplanar spacing 10,8 Å the intensity of which increases a bit at polymerization at lower temperatures, are typical for all samples of polyvinylcarbazole.

By the data of differential-thermal analysis an exothermal peak of decomposition at 480 °C is typical for the obtained samples of polyvinylcarbazole. Polymer softening point varies in the range of 280...300 °C.

As a result of kinetic investigations it is shown that the most probable polymerization mechanism in the studied system $CHCl_3$ – $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ – K is chain growth at contact or solvate separated ion pairs. Consistency of values k_P depending on initiator original concentration and proximity of its value to the known ones, referred to chain growth at ion pairs, support this [3–10].

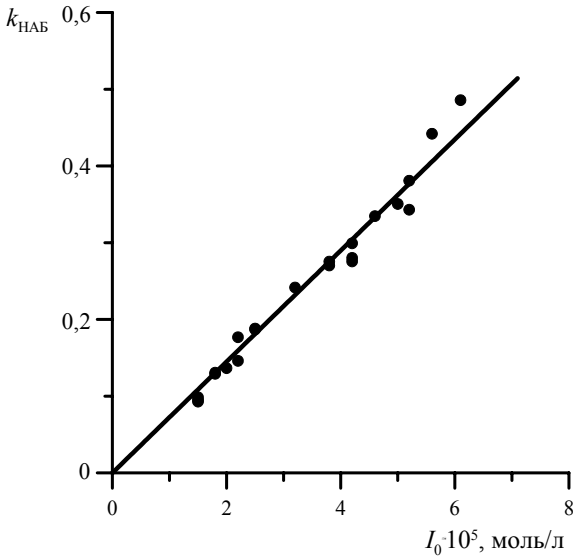

Fig. 4. *Dependence of $k_{НАБ}$ on initiator original concentration*

VC polymerization of 9-vinylcarbazole with $Ph_3C^+Al(C_2H_5)_2Cl_2^-$ as a system $CHCl_3$ – $Al(C_2H_5)_2Cl$ studied before has pronounced characteristics of «live chain» presence in the given system.

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POLYMERIZATION OF 9-ALLYLCARBAZOLE, EPOXYKARBAZOLYLPROPANE AND KARBAZOLYLTIIRAN

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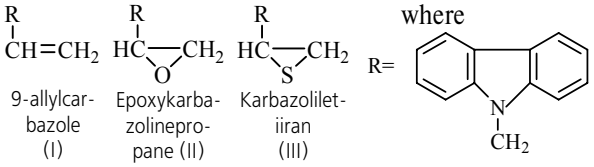
The ability to 9-allylcarbazole polymerization both with radical type activators and ion catalysts has been shown. The conditions were found and polymerization techniques of 9-allylcarbazole, 9-karbazolyltiiran and 9-epoxykarbazolylpropane were suggested.

9-allylcarbazole (9AC, I) is formed practically with quantitative output at interaction of carbazole with allyl halogenides with caustics in the medium of dipolar aprotonic solvents and may be easily refined from impurities by recrystallization from isopropyl alcohol [1].



9-allylcarbazole (I) | Epoxykarbazolinepropane (II) | Karbazolilet-iiran (III)

Structural analog of 9-allylcarbazole (I) – 9-vinylcarbazole (9VC) – is widely known owing to its polymer – polyvinylcarbazole (PVC) – the best one among organic semiconductors found wide application in nonsilver processes of recording, storing and multiplication of information. Polymerization of 9AC in comparison with 9VC is not practically studied. In short reports about the possibility of 9AC polymerization [2, 3] there was no information on conditions of process carrying out and polymer properties. It is known from scientific literature sources that allylic monomers may be polymerized by radical and ion mechanisms [4, 5]. Therefore 9AC polymerization with activator of both radical and ion type was studied. Polymerization of epoxykarbazolinepropane (EKP, II) and epiteokarbazolpropan (karbazolilet-iiran – KT, III) as possible comonomers in polymerization processes of their copolymerization with 9AC was studied parallel. Polymerization completeness was controlled by the method of thin-layer chromatography (TLC: sorbent – syluphol, eluent – benzene).

It was stated experimentally that radical polymerization of 9AC at temperature change from 60 to 100 °C and concentration of radical polymerization initiator of dinitrile azobisizooil acid (DAA) from 0,1 to 30 % from mass of loaded monomer polymerization does not occur. It is probably explained by low activity of allylic radicals in polymerization processes [5]. At temperature increase up to 100 °C the rate of polymerization rises. However parallel with formation of 9AC polymer (polyallylcarbazole, PAC) the side reactions attended by formation of karbozalylacetic acid and dikarbozalylpropanol occur. Presence of these substances was stated by the method of TLC using taps of the given substances.

EKP and KT polymerization at temperature 110 °C and addition of 30 % DAA or benzoil peroxide (BP) to monomer weight also occur. To confirm initiator participation in formation of polyepoxykarbazolylpropan